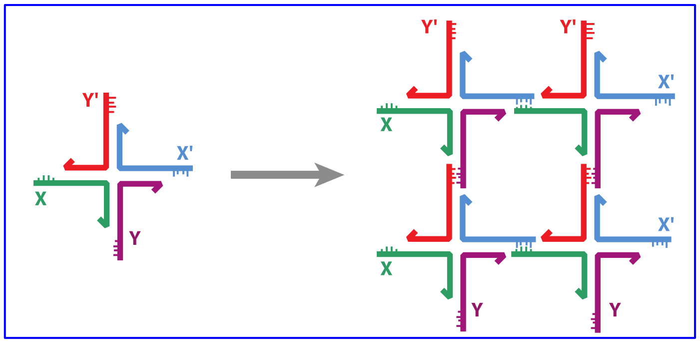
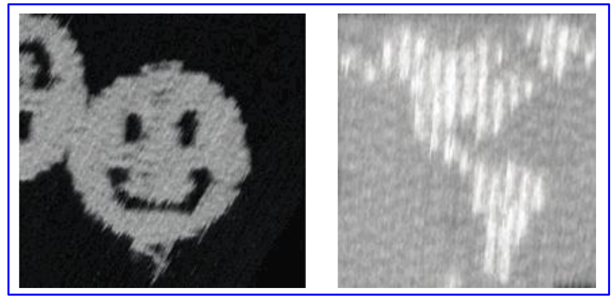
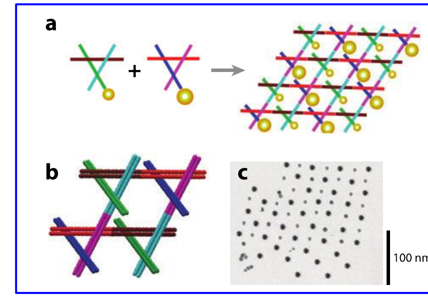
Conductive DNA Systems & Molecular Devices
ONR-MURI 2012

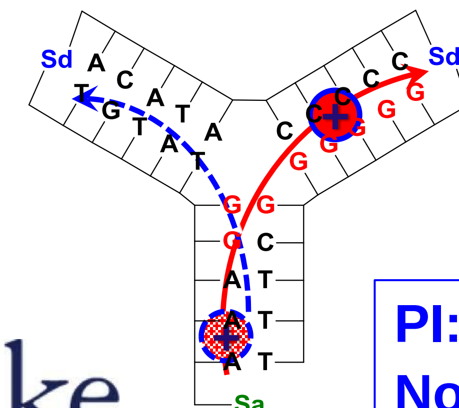
Can compelling 2D and 3D DNA assemblies like these…







… be transformed into functional electronic device elements like this?

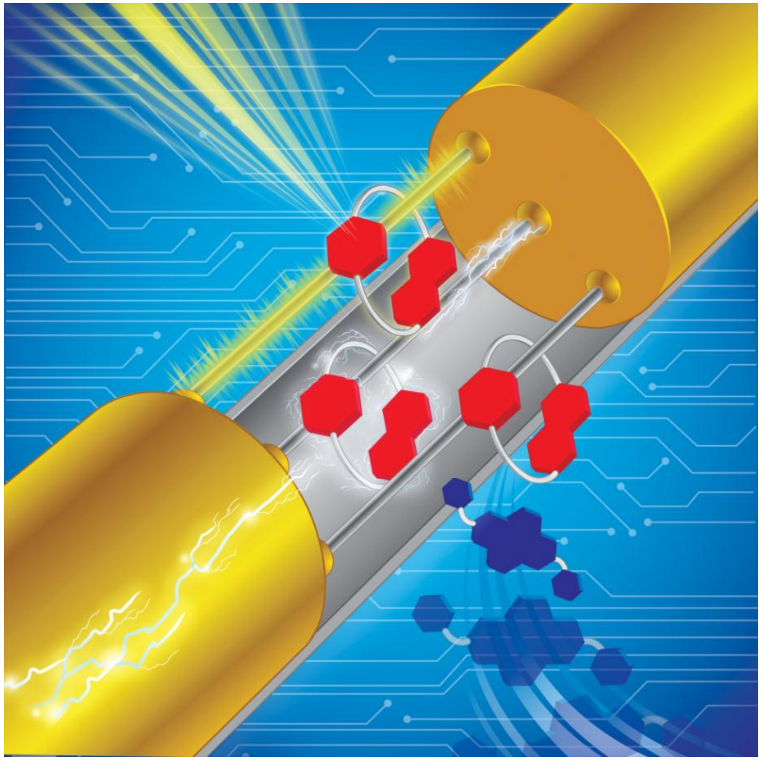


PI: Mark Ratner
Northwestern University
Presenter: David Beratan

Northwestern University · NYU · Arizona State University · Duke University

A. What are we trying to accomplish?

Design, Synthesize, Characterize, & Understand DNA-based Molecular-transport Junctions



Significance:

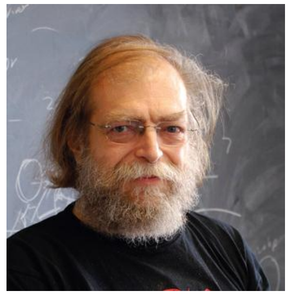
- Learning to control charge flow through novel DNA motifs;
- Designing & fabricating DNA-based elementary circuit elements & nano-sensor precursors.

Major themes:

- Design key DNA building-block structures;
- Synthesize them;
- Characterize their structure & transport;
- Study their properties in proto-devices;
- Quantify currents, elucidate control points;
- Challenge theory to establish predictive methods.

B. MURI Team Members

N. J. Tao (ASU)
3S, 1PD
Single Mol Transport



Ned Seeman (NYU)
1S, 1PD
DNA Nanotechnology

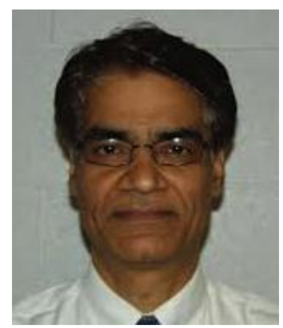
Chad Mirkin (NWU)
2S, 2PD
DNA Nanoassembly

Rajesh Naik (WP-AFB)
Bio-inspired Materials

Fred Lewis (NWU)
3PD
DNA hairpins & Ys

Mike Wasielewski (NWU) 2PD
Spin & electron acrobatics

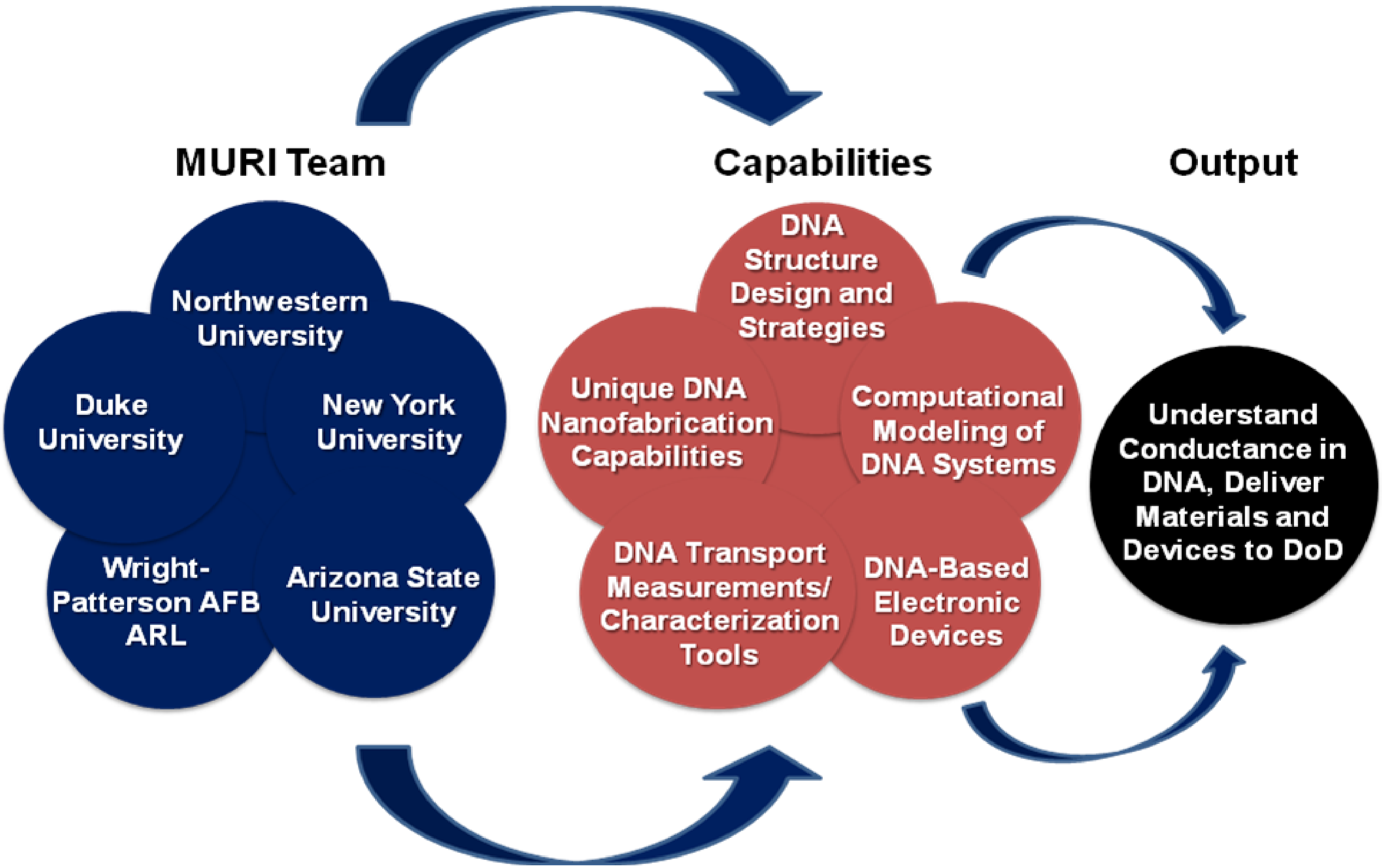
Mark Ratner, PI (NWU) 2PD
Molecular electronics theory



Sashi Karna (ARL)
Theory & simulation

David Beratan (Duke)
2S, 1PD
Theory of tunneling in macromolecules

Our Team


MURI Team
Capabilities
Output
Northwestern University
Duke University
New York University
Wright-Patterson AFB ARL
Arizona State University
DNA Structure Design and Strategies
Unique DNA Nanofabrication Capabilities
Computational Modeling of DNA Systems
DNA Transport Measurements/ Characterization Tools
DNA-Based Electronic Devices
Understand Conductance in DNA, Deliver Materials and Devices to DoD

How do we work together?

1) <u>Structure-function principles (all) and theory (Ratner, Beratan)</u> inform design & synthesis (Lewis, Mirkin, Seeman), and characterization (Tao, Wasielewski, Mirkin) of novel DNA structures and their assemblies on electrodes and in solution. Break-junctions, on-wire lithography (OWL), time-resolved optical & electron paramagnetic resonance spectroscopy elucidate function.

1) <u>Theory</u>: 1) assists in the design of the most critical structures and 2) assesses transport mechanisms (Ratner, Beratan). Where needed, theory is extended to accommodate new observations, especially in intermediate dynamical regimes. Quantum mechanics, classical molecular dynamics, and transport theory are the tools.

2) <u>Chemical synthesis (Lewis, Seeman) and molecular biology (Seeman)</u> are used to assemble small and extended DNA structures with "hooks" for break-junction and OWL transport junctions (Mirkin, Tao).

C. Principles, Prior Art, & Team

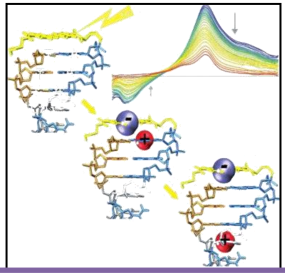
What we know:

- DNA supports tunneling and hopping transport.
- Photochemical, electrochemical, and break-junction measurements on linear structures are accessible.

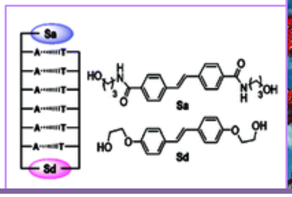
What we hope to learn:

- Are mechanisms clean or "mixed"? How do mixed mechanisms influence transport? How (and how fast) do polarons form in DNA ?
- Can we access transport in forked structures with *control points*?
- Can we make the conductivity measurements more rapid, informative, reproducible, & controlled?

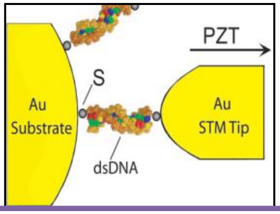
C. Principles, Prior Art, & Team



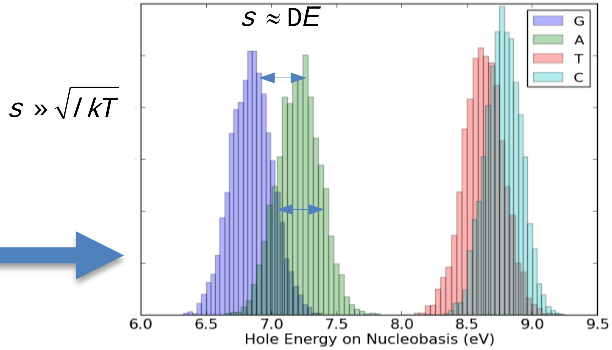
Measure charge and spin **dynamics** using time-resolved methods (Lewis, Wasielewski).



Synthesize small DNA model systems and extended constructs (Lewis, Seeman).



Measure electric **conductance** of single DNA molecules & assemblies (Tao, Mirkin).



Use theory, modeling, and computer **simulation to interpret** data & design next-generation experiments (Naik, Ratner, Beratan, Karna, Mujica).

D. Major Accomplishments to date

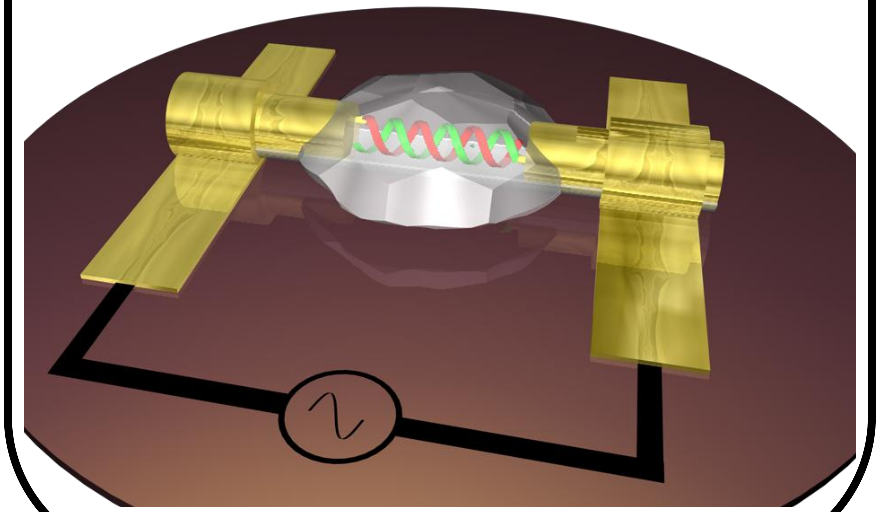
Synthesis:
- Donor-acceptor modified DNA Y-junctions, G-boxs, and linear sequences with natural and unnatural bases.
- $(CG)_n$ vs C_nG_n runs for distance dependence studies.
- Developed OWL surface functionalization methods, conducting polymer coating

Fabrication & Characterization:
- Sub-nanosecond unimolecular electron transfer kinetics measured in Y-junctions.
- Spin-dependent charge hold times measured in hairpins.
- Developed AC-tip modulation tunneling experiment to enhance sampling statistics.
- Break-junction and time-resolved spectroscopic tools are in use to characterize charge transfer currents & kinetics.

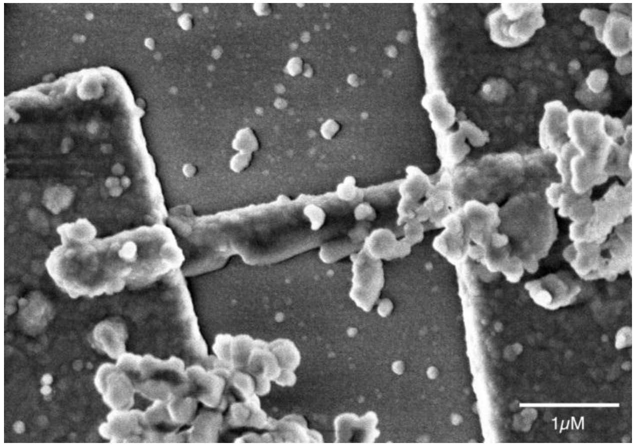
Theory, Modeling & Simulation:
- Assessment of mixed tunneling/hopping and even tunneling-free mechanisms for DNA charge transport
- Elaboration of mixed quantum classical simulations of G-box, Y-junction and linear DNA with emphasis on electrical contact across novel junctions & transport in a very “noisy” environment.
- Assessment of G-box as favorable pi-sacked coupler across strands compared to DX and related junctions.
- Detailed quantum/classical studies of tunneling/hopping & sequence dependent transport.

Major recent accomplishments.
1. SiO_2 encapsulated DNA

Synthesis of Duplex DNA Devices via Silica Encapsulation



Mirkin Group



- Substrates functionalized with a dithiolated A_{30}/T_{30} duplex and then reacted with the silica precursors to encapsulate DNA.
- I-V transport measurements do *not* show signal above noise.

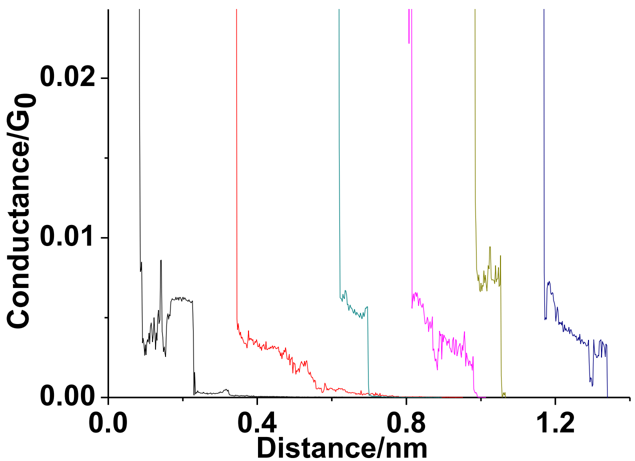
Next:

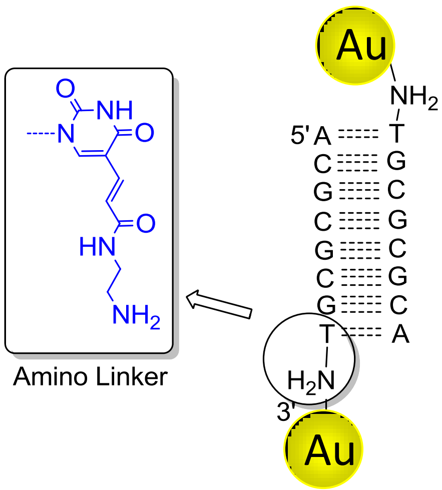
- Interrogation of the nanowires before & after SiO_2 embedding
- Resynthesize OWLs to better match DNA length
- Enhance conductivity of termini and sequence
- Modify sequences to eliminate multiple binding motifs

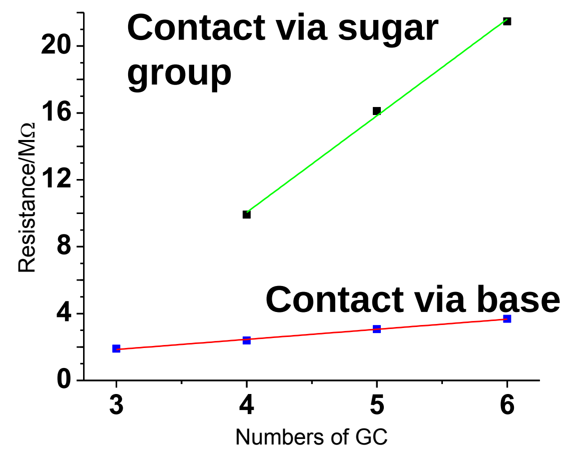
Major recent accomplishments.

2. Contact point with DNA determines distance dependence

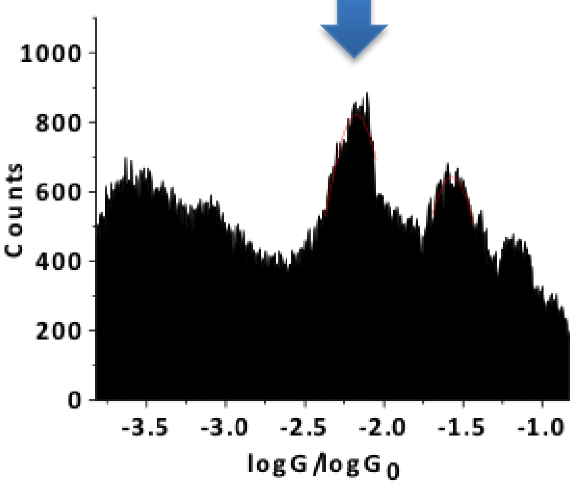
Structure of amino linker







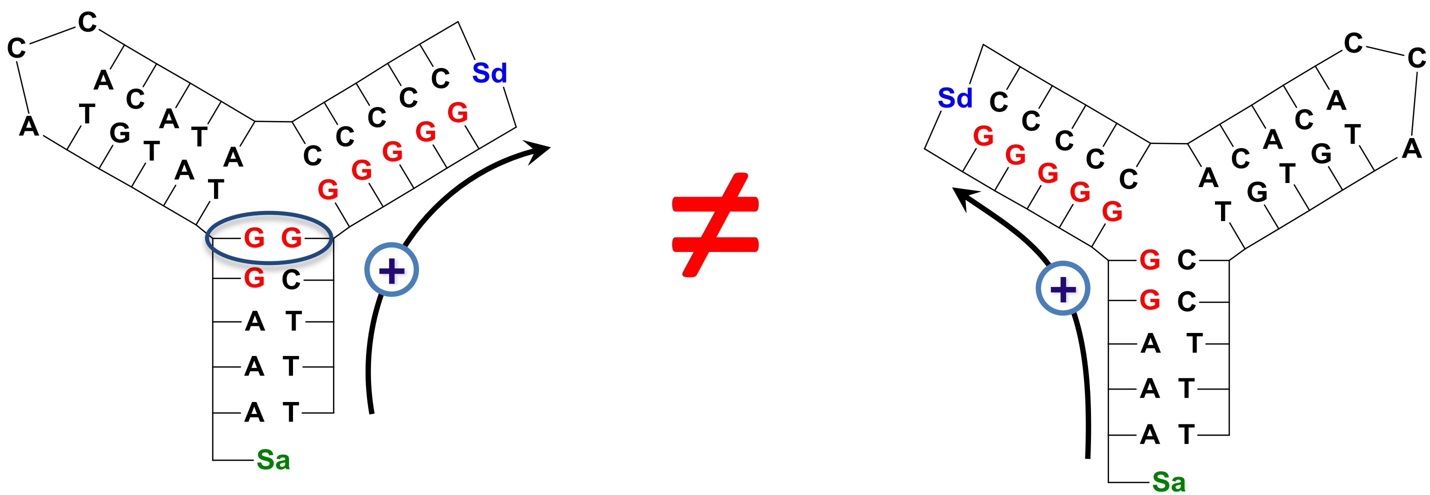
$$R = R_0 + \alpha L$$



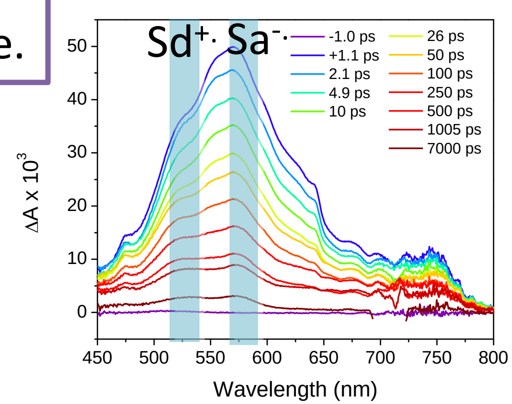
- Hopping as conduction mechanism;
- **Contact via base is ~5 times more efficient!**
- Length dependence is different (why?)

Tao Group

E. Potential breakthroughs.
1. Y-junction splitter/combiner

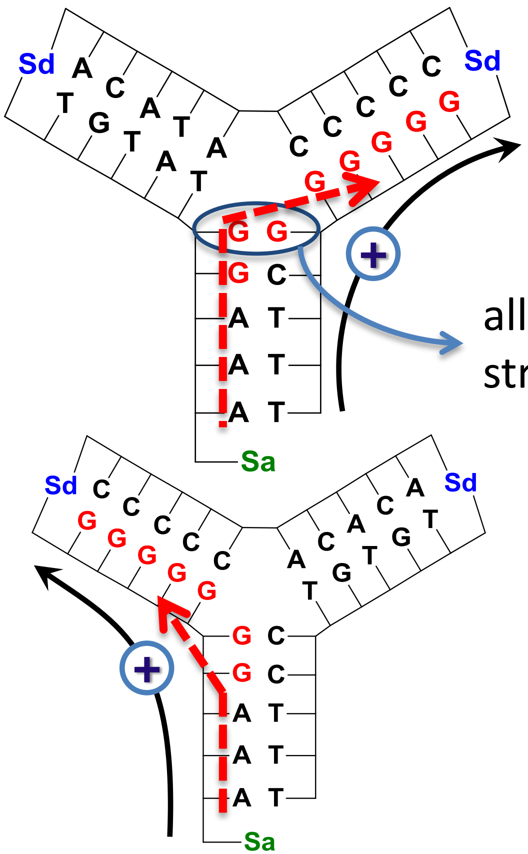


Preliminary transients indicate e- transfer from Sa to Sd in *both* species above: one arm at a time.



Wasielewski and Lewis Groups

Y-junction splitter/combiner.



allowed
strand crossing

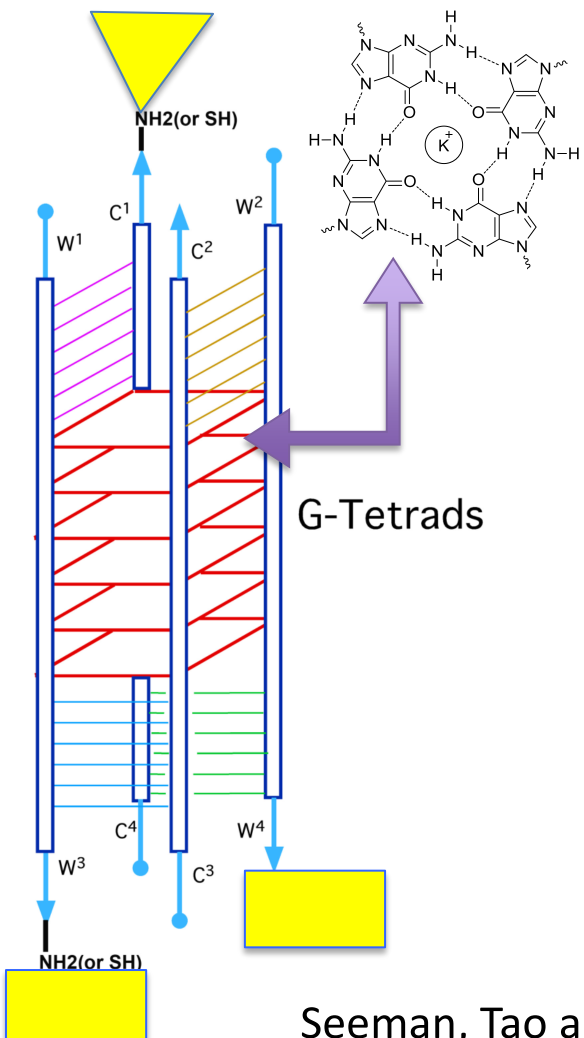
Efficient hole transport requires continuous purine A_mG_n sequence.

Strand crossing allowed for GG base pair, disallowed for GC base pair.

Under construction: 1) structures with dual ET active arms; 2) structures with multiple distinguishable S_d's.

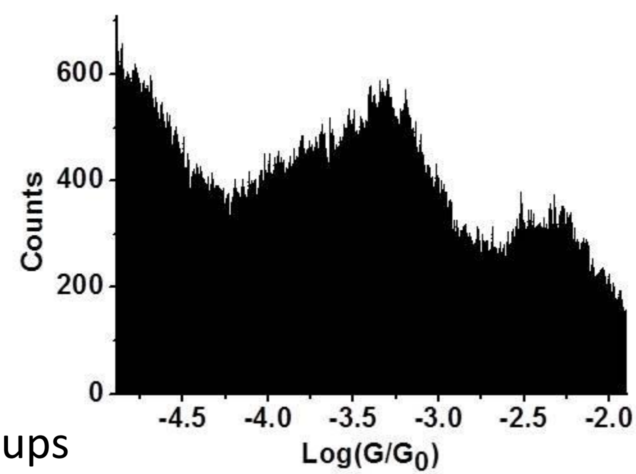
Wasielewski and Lewis Groups

Potential Breakthroughs
2. G4-box : currents splitting found



Suggested by Beratan-Tao-Seeman group discussions following initial DX-crossover analysis;
Synthesized by Seeman Group;
Measured by Tao Group.

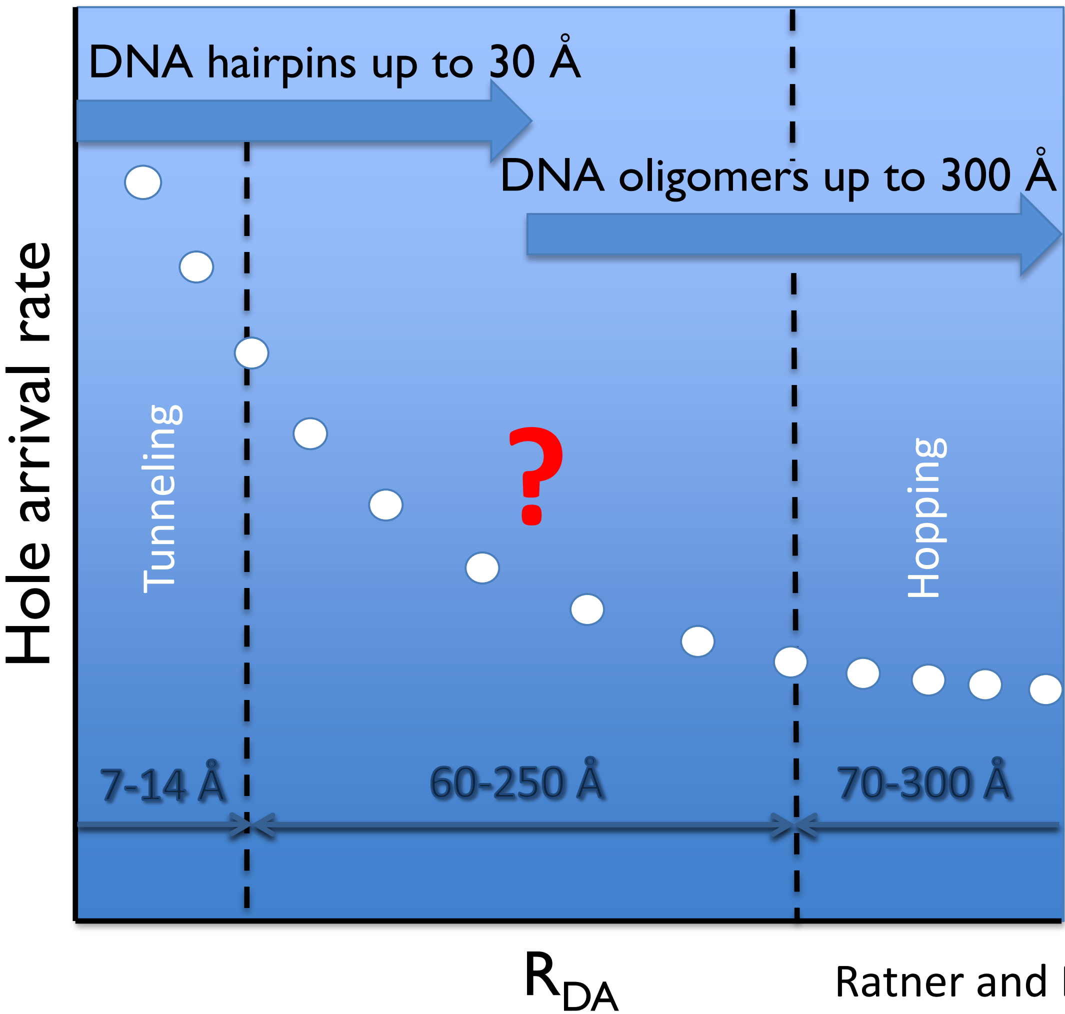
NH_2 attachments possible at W^3 ($1.4\times10^{-4}\ G_0$) & W^4 ($4.5\times10^{-4}\ G_0$);
Preliminary data show currents differ by about 3x when vary output strand positions.



Seeman, Tao and Beratan Groups

Potential Breakthroughs

3. Neither pure tunneling nor pure hopping.



Ratner Group: In intermediate distance regime, a sort of “quantum filling” occurs -- charge density fills the bridge, but polarons do not form (too little time). Agrees with Lewis , Wasielewski data.

Beratan group: in very short distance regime (≤ 4 base pairs for charge-shift reactions), multi-state resonant transport competes with tunneling. Consistent with Giese data.

Ratner and Beratan Groups

F. Why is this research significant?

1) **We demonstrated (for the first time) control of charge flow at DNA forks:**
   - We learned how to build, “wire,” interrogate, simulate, and demonstrate flow of current through BRANCHED DNA structures: Y’s and G-boxes.
   - These proof-of-principle structures may be the progenitors of self-assembling DNA transistors, single-molecule biosensors, current splitters, etc.

2) **We stretched the DNA charge transport mechanistic paradigm to include:**
   - Mixed tunneling-hopping mechanism
   - Multi-state resonance-assisted (ballistic) transport

3) **We established a strong collaborative loop among design, synthesis, characterization, analysis, and redesign:**
   - We are rapidly and cooperatively exploiting our discoveries!

G. Budgets

6/1/11 - 9/30/**11**:	$ 572,570.	
10/1/11 - 9/30/**12**:	$1,486,536.	
10/1/12 - 9/30/**13**:	$1,488,487.	
10/1/13 - 5/31/**14**:	$ 952,407.	
Initial Award:	$4,500,000.	
6/1/14 - 9/30/**14**:	$ 502,513.	Option 1
10/14/14 - 9/30/**15**:	$1,492,443.	Option 2
10/1/15 - 5/31/**16**:	$1,005,044.	Option 3
Total:	$7,500,000.	

H. Meetings & Team Interactions

- **Monthly 60 min standing video calls** among research teams.
- **July 24-25, 2011** Kick-off Meeting at Northwestern
- **October 28-29, 2012** Review at Northwestern
- **October 7-8, 2013**, Review at Northwestern
- **Frequent interactions** at ACS National Meetings and at Electron Donor-Acceptor Gordon Conference

Publications

M. Ratner team

- A. A. Voityuk, K. Siriwong, and Y. A. Berlin. Effects of various halogen anions and cations of alkali metals on energetics of excess charge recombination in stilbene donor-acceptor capped DNA hairpins. *Phys. Chem. Chem. Phys.* **2011***, 13*, 16028.
- Berlin, Y. A.; Voityuk, A. A.; Ratner, M. A. DNA Base Pair Stacks with High Electric Conductance: A Systematic Structural Search*. Nano* **2012**, *6*, 8216.
- Vayá, I.; Gustavsson, T.; Douki, T.; Berlin Y.; Markovitsi, D. Electronic excitation energy transfer between nucleobases of natural DNA. *J. Am. Chem. Soc.* **2012**, *134*, 11366.
- C. Gollub, S. Avdoshenko, R. Gutierrez, Y. A. Berlin, and G. Cuniberti. Charge migration in organic materials: Can propagating charges affect the physical quantities controlling their mobilities? *Isr. J. Chem.* **2012***, 52*, 452.
- A. Ricks, D. T. Co, K. E. Brown, M. Wenninger, S. D. Katlen, Y. A. Berlin, and M. R. Wasielewski. Exponential distance dependence of photoinitiated stepwise electron transfer in donor-bridge-acceptor molecules: Implication for wire-like behavior. *J. Am. Chem. Soc.* **2012***,* 134, 4581.
- Renaud, N.; Berlin, Y. A.; Lewis, F. D.; Ratner, M. A. Between superexchange and hopping: An intermediate charge transfer mechanism in poly(A)-poly(T) DNA hairpins. *J. Am. Chem. Soc*. **2013**, *135*, 3953.
- N. Renaud, Y. A. Berlin, and M. A. Ratner. Charge Transfer in DNA Hairpins: Impact of a Single Base Pair Substitution on the Charge Separation Rate. *Proc. Natl. Acad. Sci. USA* **2013**, submitted.

Publications, cont'd

F. Lewis team

- Carmieli, R.; Smeigh, A. L.; Mickley Conron, S. M.; Thazhathveetil, A. K.; Fuki, M.; Kobori, Y.; Lewis, F. D.; Wasielewski, M. R.: Structure and Dynamics of Photogenerated Triplet Radical Ion Pairs in DNA Hairpin Conjugates with Anthraquinone End Caps. *J. Am. Chem. Soc.* **2012**, *134*, 11251.
- Jalilov, A. S.; Patwardhan, S.; Singh, A.; Simeon, T.; Sarjeant, A. A.; Schatz, G. C.; Lewis, F. D. Structure and electronic spectra of purine-methyl viologen complexes. *J. Am. Chem. Soc.* **2013**, submitted.
- Carmieli, R.; Thazhathveetil, A. K.; Lewis, F. D.; Wasielewski, M. R.: Photoselective DNA Hairpin Spin Switches. *J. Am. Chem. Soc.* **2013,** *135*, in press**.**

C. Mirkin team

- Zhou, X.; Shade, C. M.; Schmucker, A. L.; Brown, K. A.; He, S.; Boey, F. Y. C.; Ma, J.; Zhang, H.; Mirkin, C. A. "OWL-Based Nanomasks for Preparing Graphene Ribbons with Sub-10 nm Gaps," *Nano Lett.*, **2012**, *12*, 4734.
- Schmucker, A. L.; Barin, G.; Brown, K. A.; Rycenga, M. J.; Coskun, A.; Buyukcakir, O.; Osberg, K. D.; Stoddart, J. F.; Mirkin, C. A. "Electronic and Optical Vibrational Spectroscopy of Molecular Tunnel Junctions Created by On-Wire Lithography," *Small*, **2012**, in press.
- Mangelson, B. F.; Park, D. J.; Ku, J. C.; Osberg, K. D.; Schatz, G. C.; Mirkin, C. A. "Tunable and Broadband Plasmonic Absorption via Dispersible Nanoantennas with Sub-10 nm Gaps," **2012**, in press.
- Bourret, G. R.; Ozel, T.; Shade, C.; Mirkin, C. A. "Dispersible Plasmonic and Luminescent Nanorod Dimers: Demonstration of a Long Range Plasmophore Ruler," **2012**, in press.

Publications, cont'd

N. Seeman team

- N. Nguyen, J.J. Birktoft, R. Sha, T. Wang, J. Zheng, P.E. Constantinou, S.L. Ginell, Y. Chen, C. Mao & N.C. Seeman, The Absence of Tertiary Interactions in a Self-Assembled DNA Crystal Structure, *J. Mol. Recognition* **2012,** *25*, 234.
- N. Jonoska & N.C. Seeman, Computing by Molecular Self-Assembly, *Interface Focus* **2012** *2*, 504.
- Y. Liu, R. Wang, L. Ding, R. Sha, N.C. Seeman & J.W. Canary, Templated Synthesis of Nylon Nucleic Acids and Characterization by Nuclease Digestion, *Chem. Sci.* **2012**, *3*, 1930.
- T. Wang, D. Schiffels, S. M. Cuesta, D. K. Fygenson & N. C. Seeman, Design and Characterization of 1D Nanotubes and 2D Periodic Arrays Self-Assembled From DNA Multi-Helix Bundles, *J. Am. Chem. Soc.* **2012**,*134*, 1606.
- J.E. Padilla, W. Liu & N.C. Seeman, Hierarchical Self Assembly of Patterns from the Robinson Tilings: DNA Tile Design in an Enhanced Tile Assembly Model, *Natural Computing* **2012,** *11*, 323.
- M. Ye, J. Guillaume, Y. Liu, R. Sha, R. Wang, N.C. Seeman & J.W. Canary, Site-Specific Inter-Strand Cross-Links of DNA Duplexes, *Chem. Sci.* **2013,** *4*, 1319.
- R. Sha, J.J. Birktoft, N. Nguyen, A.R. Chandrasekaran, J. Zheng, X. Zhao, C. Mao, N.C. Seeman, Self-Assembled DNA Crystals: The Impact on Resolution of 5'-Phosphates and the DNA Source, *NanoLett.* **2013**, *13*, 793.

N.J. Tao team

- S. Guo, G. Zhou, and N.J. Tao, Single Molecule Conductance, thermopower and Transition Voltage submitted Nano Lett. **2013**, submitted.
- L.M. Xiang, S. Guo, J. Palma, V. Mujica, R.A. Ratner, and N.J. Tao, Base pair stacking and even-odd length effects in single DNA conductance, **2013**, in preparation.

Publications, cont'd

M. Wasielewski team

- Carmieli, R.; Smeigh, A. L.; Conron, S. M. M.; Thazhathveetil, A. K.; Fuki, M.; Kobori, Y.; Lewis, F. D.; Wasielewski M. R. Structure and Dynamics of Photogenerated Triplet Radical Ion Pairs in DNA Hairpin Conjugates with Anthraquinone End Caps, *J. Am. Chem. Soc.* **2012**, *134*, 11251.
- Carmieli, R.; Thazhathveetil, A. K.; Lewis, F. D.; Wasielewski, M. R. Photoselective DNA Hairpin Spin Switches, *J. Am. Chem. Soc.* **2013**, *135*, in press.
- Young, R. M.; Thazhathveetil, A. K.; Lewis, F. D.; Wasielewski, M. R. Hole transport though DNA Y-Junctions, (in preparation).

D. Beratan team

- Zhang, Y.; Liu, C.; Balaeff, A.; Beratan, D.N. A Flickering Resonance Model for Charge Transport in DNA, **2013,** in preparation.
- Liu, C., Zheng, P.; Beratan, D.N., Simulating DNA-mediated Transport with White and Colored Noise Models, **2013**, in preparation.